Nitrous oxide emissions from fertilised UK arable soils: fluxes, emission factors and mitigation

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Highlights

- Nitrous oxide emissions and emission factors from 3 UK arable sites were measured
- Mitigation methods to reduce nitrous oxide emissions were investigated
- Use of the nitrification inhibitor DCD significantly reduced emissions
- Emission factors at 2 sites were much lower than the IPCC 1 % value
- Emission factors as low as 0.20 % were observed at sites experiencing low rainfall

Nitrous oxide emissions from fertilised UK arable soils: fluxes, emission factors and mitigation

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Abstract

Cultivated agricultural soils are the largest anthropogenic source of nitrous oxide (N_2O), a greenhouse gas approx.298 times stronger than carbon dioxide. As agricultural land covers 40-50% of the earth's surface agricultural N_2O emissions could significantly influence future climate. The timing, amount and form of manufactured nitrogen (N) fertiliser applied to soils are major controls on N_2O emission magnitude, and various methods are being investigated to quantify and reduce these emissions. A lack of measured N_2O emission factors (EFs) means that most countries report N_2O emissions using the IPCC's Tier 1 methodology, where an EF of 1% is applied to mineral soils, regardless of soil type, climate, or location. The aim of this research was to generate evidence from experiments to contribute to improving the UK's N_2O agricultural inventory, by determining whether N_2O EFs should vary across soil types and agroclimatic zones. Mitigation methods were also investigated, including assessing the impact of the nitrification inhibitor (NI) dicyandiamide (DCD), the application of more frequent smaller doses of fertiliser, and the impact of different rates and forms of manufactured N fertiliser. Nitrous oxide emissions were measured at one cropland site in Scotland and two in England

for 12 months in 2011/2012, along with soil and environmental variables. Crop yield was also measured, and emission intensities were calculated for the contrasting fertiliser treatments. The greatest mean annual cumulative emissions from a range of ammonium nitrate (AN) fertiliser rates were measured at the Scottish site (2301 g N_2O-N ha^{-1}), which experienced 822 mm rainfall compared to 418 mm and 472 mm at the English sites, where cumulative annual emissions were lower (929 and 1152 g N_2O-N ha^{-1}, respectively). Climate and soil mineral N influenced N_2O emissions, with a combination of factors required to occur simultaneously to generate the greatest fluxes. Emissions were related to fertiliser N rate; however the trend was not linear. EFs for AN treatments varied between sites, but at both English sites were much lower than the 1% value used by the IPCC, and as low as 0.20%. DCD reduced AN- and urea-generated N_2O emissions and yield-scaled emissions at all sites. AN application in more frequent smaller doses reduced emissions at all sites, however the type of fertiliser (AN or urea) had no impact. A significant difference in mean annual cumulative emissions between sites reflected differences in rainfall, and suggests that location specific or rainfall driven emission estimates could be considered.

Keywords

Nitrous oxide; agriculture; mineral fertilisers; emission factors; arable soil

1. Introduction

With a global warming potential 298 times greater than carbon dioxide (CO_2), nitrous oxide (N_2O) is a powerful greenhouse gas (GHG), additionally responsible for destruction of stratospheric ozone (Bhatia et al., 2010). Its potential impact on future climate is large, highlighting a requirement to identify the source and extent of N_2O emissions, and to mitigate emissions to limit our impact on climate change (Kavdir et al., 2008). Agriculture is responsible for approximately 60% of global (Bhatia et al., 2010) and 75% of the UK's (Skiba et al., 2012) anthropogenic N_2O emissions. In the UK this is a large increase on the 47% estimated in 1990 (Brown et al., 2002), mostly due to a decrease in non-agricultural (Industrial sector) N_2O emissions over this time (Defra, 2015; Skiba et al., 2012). It is clear that agriculture is not matching other sectors in emission reduction performance,

and covering 40-50% of the earth's surface (Flynn and Smith, 2010) has the potential to influence future climate. Nitrous oxide emissions in agriculture originate from many sources including manure storage and agricultural soils (Skiba et al., 2012). One of the greatest sources of emissions is 'cultivated agricultural soil' (van Groenigen et al., 2010; Regina et al., 2013), which includes direct and indirect N_2O emissions from applied manures, synthetic fertiliser application, urine deposition and crop residues. Globally these emissions are estimated to contribute to 37% of total agricultural GHG emissions, and synthetic fertiliser direct + indirect N_2O emissions are estimated to be the third largest source of GHG emissions in agriculture (Tubiello et al., 2013). In the UK, total N_2O emissions from soils are estimated to contribute between 60% (Cardenas et al., 2013) and 92% (Buckingham et al., 2014; Salisbury et al., 2014) to total agricultural N_2O emissions, with synthetic fertilisers being the largest source of these emissions (Skiba et al., 2012). Although in the UK N_2O emissions from agriculture are decreasing (Salisbury et al., 2014), with emissions from synthetic fertilisers witnessing a 17 % decline on 1990 levels in 2013 (Defra, 2015), they are increasing globally (Tubiello et al., 2013).

A reported 17% increase in global N_2O emissions from agriculture between 1990 and 2005 (Flynn and Smith, 2010) corresponds with increased nitrogen (N) fertiliser application in attempts to increase food production (Qin et al., 2012). It is estimated that in 2030 there will be global demand for 135 million tons of fertiliser N (Tilman et al., 2002; van Groenigen et al., 2010). Manufactured fertiliser N applications are essential to optimise crop yields and quality. However over-application can lead to increased N_2O emissions (Archer and Halvorson, 2010; Qin et al., 2012; Snyder et al., 2014) and potential exponential emission responses (Hoben et al., 2011). Mitigation strategies often involve reducing N supply to reduce losses to the environment (Petersen et al., 2010); however without fertilisation global food supplies would decline. With global food security a major priority the focus is on increasing the efficiency of crop production, but typically less than half of N used in agriculture is currently utilised (Oenema et al., 2009). It is apparent that a balance must be attained (Sutton et al., 2011), and methods to reduce N_2O emissions are sought. Uptake of these methods will require confidence in their performance and quantification of the reductions achievable.

Before mitigation of N_2O emissions can be introduced, quantification is required to identify key emission sources, which can vary both spatially and temporally (Desjardins et al., 2010; Regina et al., 2013), making them difficult to estimate at various scales (Regina et al., 2013). Uncertainties in N_2O emission estimates have led many countries to adopt the IPCC Tier 1 methodology. In the UK, the Emission Factor (EF1) of 1% is applied to mineral soils (IPCC, 2006), assuming that 1% of N input as fertiliser is directly emitted, regardless of soil, climate, form of fertiliser N or rate of application. Nitrous oxide emission estimates are reported as the major source of uncertainty in national GHG inventories (Leip et al., 2011); with half of all published N_2O emission inventories using this approach (Philibert et al., 2012). Although Tier 1 EFs are easy to apply, they do not reflect spatial and temporal variability, or the impact of climate (Laville at al., 2011; Kim et al., 2014). A further concern is the assumed linear increase in N_2O emissions with N application. Much evidence suggests an exponential response (McSwiney and Robertson, 2005; Cardenas et al., 2010; Hoben et al., 2011; Shcherbak et al. 2014), indicating that EFs should depend on N input rate, but the processes behind a linear/non-linear relationship are not completely understood (Kim et al., 2013).

Annual emission estimates constructed from measured data are often calculated from 15-30 measurement dates (Bouwman et al., 2002; Laville et al., 2011), but large temporal variation over an annual period means that peaks of emission can be missed and interpolation between distant points is necessary. Both of these factors mean that the annual emission based on limited measurement points has a high degree of uncertainty. Quantification of emissions is further complicated by variations dependent on the type of fertiliser applied (Regina et al., 2013). Some studies report greater emissions from nitrate- than ammonium- and urea-based fertilisers (Dobbie and Smith, 2003a; Smith et al., 2012), but there is uncertainty, with Bouwman et al. (2002) reporting greater emissions from ammonium-based fertilisers, and Li et al. (2013) reporting conflicting results. There is also evidence that N_2O emissions vary with soil N and C content (Miller et al., 2008; Tiemann and Billings, 2008; Ding et al., 2013), soil texture (Maag and Vinther, 1996), soil pH, climate, and crop type (Jones et al., 2007; Regina et al., 2013). Measurements of N_2O emissions from different climates and management systems are scarce (Laville et al., 2011; Rees et al., 2013), but if emissions vary with soil and climate

then location based EFs may improve the accuracy of N_2O emission inventories. Smith et al. (2012) considered use of the IPCC default EF to be an important weakness in emission inventories. There is a clear requirement for improved emission estimates before large-scale mitigation can be implemented. Yield-scaled emission estimates are especially important, because not only is there a need to decrease N_2O emissions, but to simultaneously increase food production (Qin et al., 2012).

In attempts to limit emissions several methods have been investigated, including applications of more frequent but smaller doses of fertiliser to avoid unutilised surplus N (Maidl et al., 1996). As denitrification and nitrification are controlled by external soil and climatic factors the time of application can also influence N_2O emissions. With maximum denitrification in temperate climates most likely to occur in late autumn to early spring (when rainfall and soil moisture are high and oxygen status low) (Cameron et al., 2013), it is often advised to avoid fertiliser application at this time. The impact of temperature, however, creates a complex situation and more research into these interactions and their influence on emissions is required. Other research has investigated reducing emissions using nitrification inhibitors (NIs) (Pfab et al., 2012), which can also potentially improve crop yields (Weiske et al., 2001; Cui et al., 2011; Di and Cameron, 2012). Reported results have been mixed (e.g. Menendez et al. 2012), although a recent meta-analysis (Abalos et al., 2014) of worldwide (predominantly) field studies concluded that N-(n-butyl) thiophosphoric triamide (NBPT, a urease inhibitor), dycandiamide (DCD, a NI) and DCD + NBPT increased crop productivity and N use efficiency (NUE) compared to the control, but with varying degrees of success for crop productivity. The study also concluded that DMPP (3,4-dimethylepyrazole phosphate) increased NUE but not crop productivity. Before they can be advocated as a robust mitigation option for use on arable land there is a requirement for more research into the environmental impact of NIs, and for N_2O emission estimates over a complete annual cycle (Pfab et al., 2012; Liu et al., 2013).

The aim of this research was to assess whether N_2O emissions are controlled by location specific soil and environmental factors, and whether the use of a universal EF of 1% for applications of N fertiliser to mineral soils is appropriate for UK conditions. In addition, the research was designed to evaluate a number of strategies to reduce N_2O emissions; *viz*, the effect of the nitrification

inhibitor, DCD, the application of more frequent smaller doses of fertiliser, and the use of different forms of inorganic N fertiliser. A further objective was to identify the relationship between fertiliser N rate and N_2O emissions.

2. Materials and methods

2.1. Field sites

Three sites were selected for emission measurements, one in Scotland and two in England, representing contrasting arable regions in the UK (Table 1). Sites were selected following a geographical assessment of UK arable land area under a range of soil/climatic zones, and a 'gap analysis' to identify zones lacking in current or planned experimental data. The location of the sites, their soil characteristics, and long-term average climate data are in Table 1. During the experiments the Gilchriston site was planted with spring barley and Rosemaund and Woburn sites with winter wheat. The crop variety, sowing and harvest date, and cropping history are also in Table 1. At each location 10 fertiliser treatments were applied (Table 2), with application rates based on guidance given in Defra's Fertiliser Manual (RB209; Defra, 2010). These vary according to crop, soil type and soil N supply status. At each site the treatments were replicated three times in a randomised block design. Plot sizes were large enough (6 m x 12 m at Rosemaund, 6 m x 10 m at Woburn, and 3 m x 10 m at Gilchriston) to allow dedicated areas for N_2O chamber placement, soil sampling and yield measurements. The yield measurement areas were 15-20 m^2 per plot, and were not disturbed apart from during the fertiliser applications.

2.2. Fertiliser application rates and dates

Fertiliser application rates for each treatment varied between sites due to the site specific standard recommended application rates (indicated in Table 2). The same number of treatments were however applied, and grouped into the following categories to enable cross-site comparison: Ammonium nitrate (AN) (lowest level, AN1), AN2, AN3, AN4, AN5 (highest level), AN split (fertiliser applied in more frequent smaller doses), urea, AN +DCD, and urea + DCD. Fertilisers were applied evenly across the plot by hand to simulate agronomic practice. Fertiliser timings were based

on commercial practice, with two applications to the spring barley at Gilchriston and three to the winter wheat at Rosemaund and Woburn. For the more frequent application treatment (AN split) the fertiliser was applied at three timings at Gilchriston and five at Woburn and Rosemaund (Table 2). For the inhibitor treatment, DCD was applied as a 2% solution at a rate equivalent to 10 kg DCD ha^{-1} one hour after fertiliser, using a knap-sack sprayer. DCD application rate was chosen to maintain consistency with other published research, and to match recommended commercial guidelines (e.g. Moir et al., 2007; de Klein et al., 2011; Moir et al., 2012). As DCD contains 65% N the amount of AN or urea applied to these plots was reduced to match the target total rate of N application. Good agricultural practice was followed throughout, with the necessary plant protection products applied at the required time.

2.3. N_2O emission sampling

Nitrous oxide emissions were measured for one year at each site from spring 2011-spring 2012 (Table 1). A closed static chamber technique was used at all sites (to maintain consistency with other similar experiments (e.g. Louro et al., 2013; Chadwick et al., 2014), where five chambers were inserted 5 cm into the soil on each plot. This gave a total of 15 replicate chambers for each treatment, and 150 chambers at each location. Circular opaque polypropylene chambers with aluminium lids were installed at Gilchriston (400 mm diameter, 300 mm height, soil surface area coverage of approximately 0.126 m^2), and square opaque polypropylene chambers at Rosemaund and Woburn (400 mm x 400 mm x 400 mm, soil surface area coverage of 0.16 m^2).

Gas sampling was undertaken between 10:00 and 12:00 each day, and focused on accounting for spatial variability of N_2O fluxes (Chadwick et al., 2014; Cardenas et al., 2010). Lids were placed onto chambers at the time of sampling, with a water filled groove or neoprene rubber on the square chambers providing an air tight seal, or by using clips to attach the aluminium lids. Chamber lids were left in place for 40 minutes, after which a syringe was used to extract a 50 ml sample of gas through a valve with a 3-way tap, and transferred to a pre-evacuated 20 ml glass vial under pressure. One sample was taken from each chamber and five ambient air samples were collected prior to chamber

188 measurements, and five at the end of the 40 minute closure period. Gas samples were returned to the
189 laboratory and a needle was used to release excess pressure within the vials. Samples were analysed
190 for N_2O concentration using an Agilent 7890A Gas Chromatograph (GC) fitted with an electron
191 capture detector (Agilent Technologies, Berkshire, UK), with a N_2O detection limit of 0.025 ppmv.
192 GC response was calibrated using certified standard N_2O gas mixtures of 0.35, 1.1, 5.1, and 10.7
193 ppmv.

194 As the crop developed, an extra chamber was stacked on top of those already in the field to
195 enable sampling without damaging the crop. All chambers were stacked at the same time, regardless
196 of whether the crop had reached the top of the chamber, to maintain consistency in the experimental
197 procedure. Once in place these extensions remained throughout the growing season. One set of
198 measurements was made in the week prior to application to provide background N_2O emissions, with
199 the sampling strategy (outlined in Table 3) then followed after each dose of fertiliser application.
200 Sampling reverted back to the start of the strategy after each application, with the aim to capture the
201 peak emissions. In addition, a further set of measurements were made in the week prior to the main
202 cultivation, immediately after cultivation, and as close to the first rain event after cultivation as
203 possible to capture any emissions generated from tillage and crop residues.

204 Calculations of N_2O flux from each chamber were made by measuring the increase in the
205 chamber headspace concentration at the end of the 40 minute period, above that of the ambient air. A
206 main assumption of the gas sampling procedure is that gas accumulation in the chamber is linear over
207 the 40 minute closure period. This was checked on each sampling occasion by selecting three random
208 chambers from the treatment with the highest N input, and is supported by evidence from earlier
209 research as part of this research programme (Chadwick et al., 2014). When checking for linearity the
210 chambers remained sealed for 60 minutes, with headspace samples taken every ten minutes.

211 *2.3.1. N_2O flux calculations*

212 Emissions of N_2O were calculated from N_2O concentrations by entering chamber closure
213 time, air temperature, and chamber height into a standardised spreadsheet used at all sites. Equations

were used to convert the change in N_2O concentrations to daily flux rates in g N_2O-N ha^{-1} d^{-1}, assuming that at one atmosphere of pressure the molar volume of an ideal gas at 15°C occupies 23.63 litres. Inclusion of air temperature in the calculation meant that an adjustment could be made to account for variation in the volume an ideal gas occupies depending on temperature. The mean flux for each plot was calculated, and plot values were used to calculate the mean flux (of three replicate plots per treatment) and standard error (SE) for each treatment. Annual cumulative fluxes were calculated by linear interpolation between sampling points, and calculation of the area under the curve. If emission measurements were a few days short of the complete annual period the flux was extrapolated to the full 365 days. A mean cumulative flux and SE was calculated for each treatment using the plot means (Supplementary tables 1-4). N_2O EFs were calculated using Equation 1, as in the IPCC methodology.

$$EF = \left(\frac{Cumulative\ \ annual\ N_2O flux\ (kg\ N_2O\text{-}N) - cumulative\ annual\ N_2O\ flux\ from\ control\ (kg\ N_2O\text{-}N)}{N\ applied\ \ (kgN)} \right) \times 100$$

Equation 1.

2.4. Crop yield

A small-plot harvester was used to harvest an area of 15 m^2 at Gilchriston, 20 m^2 at Woburn, and 20 m^2 at Rosemaund. In addition, three 1 m^2 subplots (at Gilchriston) and 6 x 50 m lengths of row (at Woburn and Rosemaund) were harvested by hand to determine the ratio of grain to straw, and to provide a sample suitable for N analysis. The dates of harvest are displayed in Table 1.

2.5. Soil mineral N

At each site, five randomly selected soil samples from the 0-10 cm layer of each plot were taken using a soil auger, and bulked to give one representative sample per plot. These topsoil samples were collected 14 times throughout the year, with an initial frequency of one per week, declining to one per month after four weeks, and then one every seven weeks after six months. Soil sampling was

planned to coincide with N_2O flux sampling. The soils were analysed for NH_4^+-N and NO_3^--N using an autoanalyser, after 2M KCl extraction of a 4 mm sieved sample (Singh et al., 2011).

2.6. Meteorological and additional soil data

Soil samples for the determination of gravimetric soil moisture content were collected on every N_2O emission sampling day. These consisted of five randomly located 0-10 cm samples from each block, which were then bulked to provide three soil moisture samples per day. Meteorological stations recorded daily air temperature and precipitation for the duration of the experiment. In addition, to provide important input data for future research using N_2O models such as DayCent (Parton et al., 2001), soil bulk density was measured on two occasions, firstly after N application and again after soil cultivation. These data were also used to convert gravimetric to volumetric moisture content and % water filled pore space (%WFPS). Further soil samples were taken at the beginning of the experiment to measure field capacity and permanent wilting point, pH (in water), extractable P, K, S and Mg, total N, TOC and particle size distribution - again to provide input data for N_2O simulation models.

2.7. Data analysis

All statistical analysis was undertaken using GENSTAT (GenStat 16th Edition. Release 16.1., VSN International Ltd., Oxford). To assess the impact of AN rate, the addition of DCD, the application of fertiliser in smaller more frequent doses, and the difference resulting from urea vs. AN, the data was grouped and analysed as follows:

1. The impact of AN rate: data analysed = Control, AN1, AN2, AN3, AN4, AN5

2. The impact of DCD addition and fertiliser type: data analysed = AN: (AN4: Rosemaund, AN3: Woburn and Gilchriston), AN + DCD, urea, urea + DCD

3. The impact of smaller, more frequent fertiliser applications: data analysed = AN: (AN4: Rosemaund, AN3: Woburn and Gilchriston), AN split

Analysis of annual cumulative emissions, grain yield, yield-scaled emissions and EFs was done using a mixed model and the REML (restricted maximum likelihood) algorithm. The random effect model was block nested within site, with a separate residual term (block by treatment interaction) for each site included when the change in deviances between the models with and without the term included indicated that it was significant. Effects of treatment, site and their interaction were tested using the Wald test. For all analysis the data was transformed to more closely satisfy the assumption that residuals and random effects are normally distributed. The type of transformation varied depending on which gave the better fit when normality of the residuals was analysed. The data were transformed using box-cox transformations (Atkinson, 1985), to determine the most suitable value of lambda to use in the transformation (where a lambda of 1 indicates no transformation, 0 = log transformation and 0.5 = square root transformation) and the equations used in the transformations are shown below Tables 4-6 respectively. Results were considered statistically significant at $p < 0.05$. Mean cumulative N_2O emissions, EFs, grain yields and yield-scaled emissions from each fertiliser treatment at each site (before removal of outliers and data transformation for statistical analysis) are displayed in Supplementary Tables 1-4.

3. Results

3.1. Weather

Total rainfall over the experimental period at Gilchriston (822 mm) was almost twice that at Rosemaund (418 mm), and much greater than that at Woburn (473 mm). This is in contrast to the 30 year average rainfall (Table 1), with all sites historically witnessing similar annual totals. There were some large singular rainfall events at Gilchriston in July, August and December 2011 (Fig. 1c), in comparison to a more even distribution at Woburn and Rosemaund (Fig. 1b and a.). Variation in daily temperature across the sites was small, with a similar annual trend at all locations. Over the experimental year, however, Gilchriston was at least 1°C cooler than the other sites, consistent with the 30 year historical temperature (Table 1). Temperatures over the experimental periods were slightly warmer than the 30 year average at all sites (Table 1).

3.2. Daily N_2O and temporal emission trends

The highest N_2O emission peak at each site was not observed until after the final fertiliser application, with only small peaks or background fluxes after the first and second applications (at Rosemaund and Woburn) or first application (at Gilchriston) (Fig. 1). Peak emissions at Rosemaund were measured on 10/05/11, seven days after the final fertiliser application, and 62 days after the first application. At Woburn peak emissions occurred 17 days after the final fertiliser application, and 73 days after the first application. Peak emissions at Gilchriston were recorded on 09/05/11, 13 days after the final fertiliser application, and 31 days after the first application. Peak N_2O emissions at Rosemaund and Woburn did not occur until soil mineral N levels had reached their maximum (Fig. 2). At Rosemaund a peak in soil NH_4^+-N on 11/05/11 coincided with the N_2O emission peak on 10/05/11, and at Woburn soil mineral N peaked on 13/05/11, followed by a peak in N_2O 13 days later on 26/05/11. Compared to these sites, there was a shorter time period between final fertiliser application and peak N_2O emissions at Gilchriston, and the peak in N_2O emissions was observed before the maximum soil mineral N levels were reached (Fig. 2).

After the first major peak in N_2O emissions, fewer N_2O emission peaks occurred at Rosemaund in the months following fertiliser application when compared to Woburn and Gilchriston despite soil mineral N remaining high for several months (Fig. 2). Although soil %WFPS fluctuated over this period it rarely exceeded 50%, and rainfall throughout May and June was very low (Fig. 1). At Woburn there was a large rainfall event on 07/05/11, and a corresponding increase in soil %WFPS from 19% to 48% (Fig. 1), but no large peak in emissions. The peak in emissions on 26/05/11 did however correspond with the next large rainfall event, also on 26/05/11, and another increase in soil %WFPS when soil mineral N had increased. Further rainfall throughout June meant that soil %WFPS remained high. After falling to 26% at the beginning of July more rainfall between 15/07/11-20/07/11 increased soil %WFPS, generating a peak in N_2O emissions. At this time soil mineral N was still above background levels (Fig. 2). Although rainfall throughout autumn and winter produced much higher levels of soil %WFPS (Fig. 1), these were not accompanied by emissions of N_2O. Emissions at Gilchriston also occurred over a prolonged period, but were greater in magnitude than at Woburn

315 (Fig. 1), with large and frequent rainfall throughout June-August, when soil mineral N was still high
316 and not limiting to emission generation. Although the major peak in N_2O emissions observed on
317 09/05/11 was not preceded by large rainfall (Fig. 1), the small amount that did occur led to an increase
318 in soil %WFPS from 29% to 51%, which appears to have been the main trigger for N_2O production,
319 when soil mineral N was high.

320

321 *3.2: The effect of AN rate*

322 *3.2.1: Annual cumulative N_2O emissions*

323 There was a significant difference in annual cumulative N_2O emissions between sites ($p = 0.007$, SED = 0.176), and a significant difference between AN fertiliser rates ($p = <0.001$, SED = 0.124), but no significant site treatment interaction (Table 4). The relative effect of AN fertiliser rate was thus consistent at all sites. The variation in measured emissions for all AN fertiliser rates at each site is illustrated in Fig. 3a. The greatest mean annual cumulative emissions were observed at Gilchriston (2301 g N_2O-N ha^{-1}), significantly greater than at Rosemaund (929 g N_2O-N ha^{-1}) and Woburn (1152 g N_2O-N ha^{-1}). There was no significant difference between the two English sites. Significantly lower mean emissions were measured from the control treatment (865 g N_2O-N ha^{-1}) than from any AN treatment. Emissions from AN2 (1171 g N_2O-N ha^{-1}) were significantly lower than from AN4 (1527 g N_2O-N ha^{-1}), AN3 (1670 g N_2O-N ha^{-1}), and AN5 (1850 g N_2O-N ha^{-1}). Emissions from AN1 were significantly lower than from AN3 and AN5, but not from AN4 or AN2. There was no significant difference in emissions from AN4, AN3 and AN5, indicating that although the greatest emissions were measured from the maximum AN rate, the relationship between AN fertiliser rate and annual cumulative emissions is not linear.

337 *3.2.2: Emission Factors*

338 There was a significant difference in annual EFs between sites ($p = 0.016$, SED = 0.279), but
339 no significant difference between AN fertiliser rates ($p = 0.081$, SED = 0.203) and no significant site

treatment interaction (Table 4). The variation in measured EFs for all rates of AN at each site is illustrated in Fig. 3b. The mean EF at Gilchriston (1.07%) was significantly greater than at Rosemaund (0.20%) and Woburn (0.33%), but there was no significant difference between the two English sites (Table 4). The mean EFs at Rosemaund and Woburn are well below the IPCC default 1% value, with the value from Gilchriston only slightly higher.

3.2.3: Grain yield

Measurements of annual grain yield revealed a significant difference between sites ($p = <0.001$, SED = 0.246), AN fertiliser rates ($p = <0.001$, SED = 0.150), and a significant site treatment interaction ($p = <0.001$, SED = 0.312) (Table 4), indicating that fertiliser application rate had a different effect on grain yield at different sites. At all sites the control produced a significantly lower grain yield than any AN application rate. At Rosemaund AN1 produced significantly lower yields than all higher AN rates, but there was no significant difference in the yield from AN2 and AN4, or between AN3 and AN4. The yield produced by AN5 was greater, but not significantly different to that from AN3. At Woburn there was no significant difference in the yield between AN1 and AN4, or between AN2 and any higher application rate. At Gilchriston AN1 and AN2 both produced significantly lower yields than all higher AN rates, but there was no significant difference in the yields from AN3, AN4 and AN5.

3.2.4: Yield-scaled emissions

There was a significant difference in yield-scaled emissions between sites ($p = <0.001$, SED = 0.241), and between AN fertiliser rates ($p = <0.001$, SED = 0.180), but no significant site treatment interaction (Table 4). The relative effect of AN fertiliser rate was thus consistent at all sites and is illustrated in Fig. 3c. Yield-scaled emissions were significantly lower at Rosemaund (0.12 g N_2O-N kg^{-1} DM) than Woburn (0.27 g N_2O-N kg^{-1} DM) and Gilchriston (0.50 g N_2O-N kg^{-1} DM), and those from Woburn were significantly lower than from Gilchriston. In relation to the difference between treatments, yield-scaled emissions were significantly greater from the control than from all AN

365 applications. The only significant difference between AN application rates was greater emissions from
366 AN1 (0.27 g N_2O-N kg^{-1} DM) than from AN2 (0.19 g N_2O-N kg^{-1} DM).

367

368 *3.3: The impact of DCD addition and fertiliser type*

369 *3.3.1: Annual cumulative N_2O emissions*

370 There was a significant difference in annual cumulative N_2O emissions between fertilisers
371 with and without DCD ($p = 0.027$, SED = 0.123), but not between sites ($p = 0.094$), or between urea
372 and AN fertilisers ($p = 0.72$) (Table 5). The lack of any significant interaction between site and the
373 addition of DCD, between fertiliser type and the addition of DCD, and between site and fertiliser type
374 indicates that DCD significantly reduced annual cumulative emissions at all sites, and when applied to
375 both AN and urea fertiliser, and that emissions from urea and AN did not differ at any site. The
376 variation in emissions for all treatments at each site is illustrated in Fig. 4a. Greatest mean annual
377 cumulative emissions were observed from fertilisers without DCD (1476 g N_2O-N ha^{-1}), compared to
378 a mean flux from fertilisers with DCD, of 1121 g N_2O-N ha^{-1}.

379 *3.3.2: Emission Factors*

380 Fertilisers with DCD produced a significantly lower EF than those without ($p = 0.018$) but
381 there was no significant difference in EFs for the different sites ($p = 0.180$), or between urea and AN
382 fertiliser ($p = 0.947$). A significant interaction between fertiliser type and the presence/absence of
383 DCD ($p = 0.014$, SED = 0.237) (Table 5) indicates that DCD only reduced the EF when added to AN
384 fertiliser, with an EF of 0.06% for AN+DCD, significantly less than 0.55% for AN. Low emissions
385 from urea + DCD and high emissions from the control plots resulted in the calculation of two large
386 negative EFs at Gilchriston. Exclusion of these outliers from the analysis can explain why this
387 significant interaction was observed in relation to EFs, but not to cumulative emissions. The lack of
388 any interaction between site and DCD, or between site and fertiliser type, indicates that AN with DCD

had a lower EF than AN at all sites, and that EFs for urea and AN do not differ at any site. The variation in EFs for all treatments at each site is displayed in Fig. 4b.

3.3.3: Grain yield

There was a significant difference in grain yield produced from fertilisers with or without DCD (p = <0.001), at different sites (p = <0.001), and from AN and urea (p = 0.019). There was also a significant interaction between site and fertiliser type (p = 0.043, SED = 0.091), and between site and the presence or absence of DCD (p = 0.017, SED = 0.091) (Table 5). At Rosemaund and Gilchriston there was no significant difference between grain yield produced from AN and urea, but at Woburn a significantly greater yield was produced from AN (5.65 t ha^{-1}) than urea (4.69 t ha^{-1}). There was no interaction between the type of fertiliser and the presence/absence of DCD, indicating that DCD had the same effect on grain yield whether applied with urea or AN. The variation in grain yield for all treatments at each site is displayed in Fig. 4c.

3.3.4: Yield-scaled emissions

Comparison of yield-scaled emissions revealed a significant difference between fertilisers with or without DCD (p = 0.044, SED = 0.0724), and between sites (p = <0.001, SED = 0.128), but not between fertiliser type (p = 0.896). There were no significant interaction effects (Table 5). Yield-scaled emissions were significantly lower when DCD was added to the fertiliser (0.17 g N_2O-N kg^{-1} DM) than without DCD (0.22 g N_2O-N kg^{-1} DM), and were significantly lower from Rosemaund (0.098 g N_2O-N kg^{-1} DM) than from Woburn (0.22 g N_2O-N kg^{-1} DM) and Gilchriston (0.30 g N_2O-N kg^{-1} DM). There was no difference between those from Woburn and Gilchriston. The lack of any significant interactions indicates that this reduction in yield-scaled emissions with DCD was true at all locations, and when applied to either type of fertiliser (Fig. 4d).

3.4: The effect of more frequent but smaller fertiliser applications

3.4.1: Annual cumulative N_2O emissions and EFs

There was a significant difference between emissions from AN and emissions from AN applied in more frequent smaller doses ($p = 0.023$, SED = 0.041), and between sites ($p = 0.003$, SED = 0.187), but no interaction effect (Table 6, Fig. 4a). Emissions from AN split were significantly lower (1472 g N_2O-N ha^{-1}) than from AN (1705 g N_2O-N ha^{-1}), and emissions from Gilchriston (3057 g N_2O-N ha^{-1}) were significantly higher than from Rosemaund (974 g N_2O-N ha^{-1}) and Woburn (1388 g N_2O-N ha^{-1}), but there was no significant difference between emissions from Rosemaund and Woburn (Table 6). As with annual cumulative emissions, there was a significant difference in EFs from AN and AN split ($p = 0.014$, SED = 0.0565), and between sites ($p = 0.005$, SED = 0.3639) (Table 6). The lower EF for AN split treatments was observed at all sites (Fig. 4b).

3.4.2: Grain yield and Yield-scaled emissions

There was a significant difference in grain yield between sites ($p = <0.001$, SED = 0.381), but no significant difference resulting from the application of fertiliser in more frequent smaller doses ($p = 0.082$) (Table 6). Calculation of yield-scaled emissions revealed a significant difference between sites ($p = <0.001$, SED = 0.381), but not resulting from the application of fertiliser in more frequent smaller doses ($p = 0.129$) (Table 6). The variation in grain yield and yield-scaled emissions is displayed in Fig. 4 c and d.

4. Discussion

The mean annual cumulative emission of 3.25 kg N_2O-N ha^{-1} from the current recommended fertiliser rate (180 kg N/ha) at Gilchriston (Table 4) is more than 1 kg ha^{-1} greater than the 2.1 kg N_2O-N ha^{-1} quoted by Sozanska et al. (2002) from cereal crops in Britain. Lower values of 1.50 kg N_2O-N ha^{-1} and 1.04 kg N_2O-N ha^{-1} measured at Woburn and Rosemaund however, emphasise large variation and a clear difference in annual cumulative N_2O emissions between sites. Although high N_2O emissions from the Scottish site suggest regional variations, rainfall appears to be a major control. This is supported by Flynn et al. (2005) who argue that “transient properties” not “permanent soil features” are largely responsible for a variation in emissions, and similar studies that have

ascribed low fluxes to unusually dry conditions (Louro et al., 2013). Dobbie et al. (1999) also found rainfall and temperature to have the greatest influence on N_2O, and strong relationships between %WFPS and N_2O emissions are reported in Garcia-Marco et al. (2014). However, whilst the locations during these experiments received contrasting rainfall, the comparison of only three sites means that the impact of other soil variables is difficult to determine, and requires further investigation. This call for more research is supported by observations of higher fluxes from soils with a greater SOC content (Harrison-Kirk et al., 2013), and variations caused by soil pH (Lesschen et al., 2011), both of which could explain higher emissions at Gilchriston. The role of SOC though remains uncertain, with Webb et al. (2014) arguing that recent inputs of active SOC rather than total SOC activate microbial activity, of which the majority of the measured SOC is comprised. Interactions between carbon addition, soil compaction and N_2O emissions were reported in Garcia-Marco et al. (2014). The role of soil texture and its influence on emissions must also be considered, with free-draining soils retaining less water and likely to undergo less denitrification (Cameron et al. 2013).

The role of other variables and the complex nature of N_2O emission generation is revealed in analysis of the daily N_2O flux data, and further highlighted by Luo et al. (2013) who failed to find strong relationships between either soil moisture or soil temperature and N_2O release, suggesting that simple relationships between these variables are not often observed in long term studies such as this. At all sites in this study large fluxes were observed when a combination of driving factors occurred simultaneously, and when thresholds were crossed, with strong evidence of the combined role of soil N levels, rainfall and soil %WFPS. The delay in peak N_2O emissions until after the final application of fertiliser at all sites suggests that some soil or environmental factors required for emission generation were limiting until this time. This can partly be explained by the smaller application rates in the earlier doses (Table 2), and thus the lower level of soil mineral N available for nitrification and denitrification until after the final application, but also by the rainfall and soil moisture status at these times. The fact that the time lag between final fertiliser application and peak N_2O emissions was shortest at Gilchriston suggests either a lower mineral N threshold for N_2O production at this site, or that other environmental thresholds were crossed before soil N had peaked at this site, allowing the

467 production of N_2O (also see Hinton et al., 2015). Although soil mineral N remained high at
468 Rosemaund after fertiliser application it was not accompanied by further N_2O emission peaks,
469 indicating that other limiting factors, in particular rainfall, must have prevented the production of
470 N_2O, emphasising the complex nature of this process. This is further supported by Rees et al. (2013),
471 who found poor relationships between single variables and emissions, with Harrison-Kirk et al. (2013)
472 suggesting that emissions are controlled by a "complex set of factors". At all three sites in this study
473 although more frequent rainfall and very high levels of soil %WFPS were observed in winter (Fig. 1),
474 the decline in soil mineral N to background levels by this time (Fig. 2) meant that this was now the
475 limiting factor in N_2O emission generation.

476 The results of this study suggest that a uniform EF should not be assumed for the whole of the
477 UK. However a move towards location specific EFs would require the variation in emissions observed
478 in these experiments to be replicated when rainfall at all locations is more typical of the long-term
479 average. Rainfall at Gilchriston greatly exceeded the 30 -year mean annual rainfall figure during this
480 experiment, whilst rainfall at the other sites was below average (Table 1). More emission
481 measurements and corresponding estimates of EFs are thus required at times of high and low rainfall,
482 and from various locations. Ideally emissions at all sites should be measured for multiple annual
483 periods to gain a true reflection of each site. A further improvement on predicting emissions could
484 involve the modelling of emissions based on rainfall, %WFPS and soil mineral N, and the data
485 gathered from these experiments can be used to help calibrate simulation models from which EFs
486 could be generated for more typical weather conditions. The implication of greater N_2O emissions
487 following periods of high rainfall and high soil moisture is important, not only in predicting current
488 global emissions on a spatial scale, but also emission trends into the future, with autumn and winter
489 rainfall in the UK and Ireland expected to increase by between 14 and 25 % towards the end of the
490 century (Kim et al., 2014; Defra, 2009).

491 Although there was a significant difference in N_2O emissions due to varying AN rates, this
492 increase was not linear, with little increase beyond those generated using current recommended
493 fertiliser rates. These results do not support those of previous arable and grassland site studies

494 (McSwiney and Robertson, 2005; Cardenas et al., 2010; Hoben et al., 2011) in which an exponential
495 increase in emissions was observed with increasing N application rates. The very low emissions from
496 all AN rates at the English sites (due to the unusually dry conditions) mean that a difference in
497 emissions with fertiliser rate would be hard to detect. Further investigations under contrasting rainfall
498 conditions are required, as emissions generated in wetter conditions may reveal a stronger relationship
499 between them and application rate. Although these results suggest that N_2O emissions will be no
500 greater at AN application rates above those used in current practice, applying AN at higher rates
501 would be of questionable benefit, due to the lack of a significant increase in yield with higher rates,
502 supporting previous research described by Qin et al. (2012), where medium rates of N fertiliser
503 resulted in the most efficient yield-scaled emissions. Although this threshold varied slightly between
504 sites, there is a general indication that application rates above AN3 (180 kg N ha^{-1} at Rosemaund; 180
505 kg N ha^{-1} at Woburn; 120 kg N ha^{-1} at Gilchriston) will be inefficient. However, the lack of any
506 significant increase in N_2O emissions once this application rate is exceeded suggests that N is not
507 being released to the atmosphere as N_2O, warranting further research into other N loss pathways.
508 Greater emissions per kg of dry matter from the control than from any AN fertiliser rate indicate that
509 it is beneficial to apply fertiliser, with lowest emissions from AN2 suggesting that application rates
510 slightly below current recommended practice (AN4 at Rosemaund and AN3 at Woburn and
511 Gilchriston) may be the most beneficial when both crop production and N_2O emissions are
512 considered.

513 A lack of any significant difference in EFs between the different rates of AN or types of N
514 fertiliser used in this study suggests that the IPCC approach of using a default value for all levels of
515 fertiliser at a specific location is acceptable; however the value of 1% could be reconsidered, and
516 could vary with location. The variation in EFs between sites, and deviation from 1% is supported by
517 other research which argues that the IPCC approach of using a universal EF is not sufficient, and that
518 different crops, soils and climates should have different EFs (Flynn et al., 2005; Flynn and Smith,
519 2010). These results support the arguments of Halvorson and Del Grosso (2013) that the current EF of
520 1% may be too high, but large values reported in other studies indicate that further work is required

521 before a firm consensus can be reached. Stehfest and Bowman (2006) report a range in EFs from 0-
522 30.4% for AN fertilisers, based on a review of 131 studies, and EFs from urea fertiliser as high as
523 46.44%. Similarly, Buckingham et al. (2014) in a review of non-UK data relevant to UK conditions,
524 report EFs from −0.34% to 37%. Higher EFs (6.5%) for AN fertilisers specific to the UK are also
525 reported by Dobbie and Smith (2003b).

526 In relation to N_2O emission mitigation, the use of DCD was successful at all sites when
527 applied to both AN and urea fertilisers. These findings support reported emission reductions of 39-
528 81% (Misselbrook et al., 2014; Cameron et al., 2014; McTaggart et al., 1997; Shoji et al., 2001), but
529 conflict with those where no significant reductions were found (Barneze et al., 2015; Bell et al., 2015;
530 Watkins et al., 2013). The location of the study, the length of the experiment, and the weather
531 conditions at the time of the experiment are important factors to consider when assessing the
532 performance and success of DCD. The studies of Barneze et al. (2015) and Bell et al. (2015) are
533 specific to UK grasslands, and Watkins et al. (2013) to New Zealand grasslands, with all relating to
534 the use of DCD added to animal urine, often when temperatures were high and likely to have caused
535 rapid degradation of the DCD. Misselbrook et al. (2014) and McTaggart et al. (1997) also
536 demonstrate the variation in DCD performance depending on the type of N fertiliser to which DCD is
537 applied. The conflicting results presented in the literature suggest that the performance of DCD
538 should be assessed in relation to the specific land-use and environment in which it will be applied, and
539 that more research is required before the results from grasslands and urine application can be assumed
540 to also apply to UK arable land, and *vice versa*. The risk of DCD leaching into surface and ground
541 waters, and blocking the beneficial process of nitrification in aquatic systems is also highlighted in
542 recent research, and will require more investigation before the use of DCD can be encouraged on a
543 large scale (Smith and Schallenberg, 2013). The observed decrease in yield-scaled emissions does
544 however indicate the potential of DCD as a mitigation mechanism, deserved of much further research.
545 The lack of any significant difference in cumulative emissions between AN and urea fertiliser at any
546 site is in contrast to previous research, and does not support other studies that have found greater
547 emissions from urea (Flynn and Smith, 2010) or those that have reported reduced emissions due to

548 ammonia volatilisation (Smith et al., 2012). The lower yields at Woburn from urea fertilised plots
549 could however be the result of ammonia volatilisation, which can be as much as 20% higher from
550 urea than AN fertiliser (Chambers and Dampney, 2009), resulting in less N available to the crop,
551 suggesting that further research into N loss pathways from different N fertiliser types is required.
552 Although the application of fertiliser in smaller more frequent doses reduced emissions, and has the
553 potential to be considered as a mitigation option, the lack of any reduction in yield-scaled emissions
554 calls for further research.

555 **5. Conclusions**

556 A significant difference in mean annual cumulative N_2O emissions between sites with
557 contrasting rainfall indicates that location specific emission estimates could be considered, and
558 reinforces the suggestion that N_2O emissions from N fertiliser depend on weather, local climatic, and
559 soil characteristics. Relationships between N_2O emissions, rainfall and soil moisture suggest that a
560 further improvement to emission estimation would involve the use of modelling to simulate the
561 influence of these variables on emissions. EFs calculated for all three sites and for urea and AN
562 fertiliser suggest that use of a constant value for all the forms and rates of fertiliser N we used is
563 acceptable, but EFs much lower than the IPCC 1% default observed under very low rainfall at the two
564 English sites imply that a reduction on this value may be required for certain locations or conditions.
565 Emission reductions resulting from the use of the NI, DCD, and split fertiliser applications highlight
566 their potential as N_2O emission mitigation tools warranting further investigation, especially in regard
567 to their impact on crop yield and yield-scaled emissions.

568

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800 # Figure Captions

801 **Fig. 1.** Daily variation in N_2O emissions, rainfall and %WFPS at **a.** Rosemaund; **b.** Woburn; **c.**
802 Gilchriston. Solid arrows represent times of fertiliser application; dashed arrows indicate the timing of
803 additional doses applied in AN split treatments. (Note different Y axes for Daily Mean N_2O flux and
804 %WFPS between a, b and c). Error bars represent the SE of the mean.

805 **Fig. 2.** Annual variation in soil NH_4^+-N, soil NO_3^--N contents and N_2O emissions at: **a.** Rosemaund;
806 **b.** Woburn; **c.** Gilchriston. Solid arrows represent times of fertiliser application; dashed arrows
807 indicate the timing of additional doses applied in AN split treatments. (Note different Y axes between
808 a, b and c).

Fig. 3a. Variation in measured annual cumulative N_2O emissions for all rates of AN fertiliser at each of the three arable sites (n = 3); **b.** Variation in measured EFs for all rates of AN fertiliser at each of the three arable sites (n = 3. Two outliers removed from analysis from Gilchriston AN1, one outlier removed from Gilchriston AN2); **c.** Variation in measured yield-scaled emissions for all rates of AN fertiliser at each of the three arable sites (n = 3). Fertiliser descriptions are contained in Table 2. Crossed circles represent the mean, horizontal lines represent the median, vertical boxes represent the interquartile range.

Fig. 4a. Variation in measured annual cumulative N_2O emissions for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3); **b.** Variation in measured EFs for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3. Two outliers removed from analysis from Gilchriston Urea + DCD); **c.** Variation in measured grain yield for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3); **d.** Variation in measured yield-scaled emissions for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3). Fertiliser descriptions are contained in Table 2. Crossed circles represent the mean, horizontal lines represent the median, vertical boxes represent the interquartile range

843

844 **Table 1.** Environmental, soil and crop data/characteristics for the three arable experimental sites.

	Rosemaund	Woburn	Gilchriston
Location	Hereford, England	Bedfordshire, England	East Lothian, Scotland
Grid reference	SO536 464	SP948 353	NT479 658
Altitude (m)	75	96	160
Total precipitation over experimental period (mm)	418	473	822
Mean temperature over experimental period (°C)	10.4	10.9	9.4
30 year average annual precipitation (mm)	657 (1970 - 1999)	652 (1981 - 2010)	676 (1971 - 2000)
30 year average annual temperature (°C)	9.4 (1970 - 1999)	9.9 (1981 - 2010)	8.6 (1971 -2000)
Soil pH	6.50	7.05	6.30
Soil organic carbon (%)	1.00	0.96	1.26
Soil bulk density (0-10 cm) (g/cm^3)	1.24	1.61	1.36
Soil texture	Clay loam	Loamy sand over sandy loam	Sandy clay loam
Soil particle size distribution	Sand: 27 % Silt: 52 % Clay: 21 %	Sand: 66 % Silt: 23 % Clay: 11 %	Sand: 66 % Silt: 21 % Clay: 13 %
Crop type	Winter Wheat (var. Alchemy)	Winter Wheat (var. Oakley)	Spring Barley (var. Optic)
Sowing date	05/10/10	20/10/10	22/03/11
Tillage date	20/09/10	20/10/10	
Harvest date	11/08/11	02/09/11	22/08/11
Cropping history (1 year before experiment)	Winter Oats	Winter Beans	Spring Barley
Cropping history (2 years before experiment)	Winter Wheat	Winter Wheat	Winter Wheat
Measurement period	08/03/11 - 07/03/12	11/03/11 - 10/03/12	07/04/11 - 06/04/12

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847 **Table 2.** Fertiliser application rates (kg N ha^{-1}) at the 3 experimental sites. AN = ammonium nitrate;
848 DCD = dicyandiamide. Numbers in brackets indicate the amount of fertiliser applied on each
849 application date. Dates underlined refer to the additional application dates for the AN split treatment.
850 Numbers in bold indicate the current recommended application rates for each location.

Fertiliser	Rosemaund	Woburn	Gilchriston
Control	0	0	0
AN 1	60 (20, 20, 20)	60 (20, 20, 20)	40 (20, 20)
AN 2	120 (40, 40, 40)	120 (40, 40, 40)	80 (40, 40)
AN 3	180 (40, 70, 70)	**180** (40, 70, 70)	**120** (40, 80)
AN 4	**240** (40, 100, 100)	240 (40, 100, 100)	160 (40, 120)
AN 5	300 (40, 130, 130)	300 (40, 130, 130)	200 (40, 160)
AN split	240 (40, 50, 50, 50, 50)	180 (40, 40, 40, 30, 30)	120 (40, 40, 40)
Urea	240 (40, 100, 100)	180 (40, 70, 70)	120 (40, 80)
AN + DCD	240 (40, 100, 100)	180 (40, 70, 70)	120 (40, 80)
Urea + DCD	240 (40, 100, 100)	180 (40, 70, 70)	120 (40, 80)
Application dates	09/03/11, 04//04/11, 18/04/11, 03/05/11, 16/05/11	14/03/11, 11/04/11, 26/04/11, 09/05/11, 23/05/11	08/04/11, 26/04/11, 04/05/11

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854 **Table 3.** N_2O emission sampling schedule

Weeks after each fertiliser application	Number of N_2O emission measurements
-1	1
0	5
1	5
2	2 (evenly spaced through the week)
3	2 (evenly spaced through the week)
4-7	2 (evenly spaced)
8-12	2 (evenly spaced)
13-16	2 (evenly spaced)
17-20	2 (evenly spaced)
21-24	2 (evenly spaced)
25-28	1
29-32	1
33-36	1
37-40	1
41-44	1
45-48	1
49-52	1

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Table 4. The impact of AN fertiliser rate, site and their interaction on annual cumulative N_2O emissions, EFs, grain yield, and yield-scaled emissions: Transformed and back transformed values. When a significant effect is present, transformed values that do not share a letter are significantly different. R = Rosemaund; W = Woburn; G = Gilchriston. AN = ammonium nitrate. Treatment rates are displayed in Table 2. Details of the transformations applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Site/treatment	Cumulative N_2O emissions (kg N_2O-N ha^{-1})		EF (%)		Grain yield (t ha^{-1})		Yield-scaled emissions (g N_2O-N kg^{-1} DM)	
	Transformed[1]	Back transformed	Transformed[2]	Back transformed	Transformed[3]	Back transformed	Transformed[4]	Back transformed
R	-0.07 [a]	0.93	-1.06[a]	0.20	5.36	8.02	-2.63[a]	0.12
W	0.14 [a]	1.15	-0.82[a]	0.33	2.93	4.52	-1.49[b]	0.27
G	0.77 [b]	2.30	0.11[b]	1.07	3.52	5.33	-0.75[c]	0.50
Control	-0.15 [a]	0.87	N/A	N/A	1.20	2.32	-1.03[c]	0.39
AN1	0.19 [bc]	1.21	-0.25	0.72	2.90	4.48	-1.49[b]	0.27
AN2	0.16 [b]	1.17	-0.81	0.33	4.23	6.34	-1.99[a]	0.19
AN3	0.49 [d]	1.67	-0.48	0.54	5.13	7.67	-1.77[ab]	0.22
AN4	0.41 [cd]	1.53	-0.74	0.37	4.80	7.18	-1.78[ab]	0.22
AN5	0.58 [d]	1.85	-0.67	0.41	5.36	8.02	-1.69[ab]	0.23
Control-R	-0.43	0.66	N/A	N/A	2.50[bc]	3.95	-2.15	0.17
Control-W	-0.33	0.73	N/A	N/A	0.85[a]	1.91	-1.07	0.38
Control- G	0.32	1.39	N/A	N/A	0.24[a]	1.24	0.12	1.13
AN1-R	-0.1	0.91	-0.71	0.39	4.15[ef]	6.23	-2.34	0.15
AN1-W	0.12	1.13	-0.26	0.72	2.49[bc]	3.94	-1.42	0.29
AN1-G	0.54	1.77	-0.32	0.67	2.07[b]	3.39	-0.70	0.52
AN2-R	0.00	1.00	-0.99	0.24	5.66[hi]	8.48	-2.67	0.12
AN2-W	-0.08	0.92	-1.34	0.10	3.44[de]	5.22	-2.05	0.18
AN2-G	0.55	1.79	-0.15	0.81	3.58[de]	5.42	-1.24	0.33
AN3-R	0.02	1.02	-1.12	0.18	6.81[jk]	10.28	-2.94	0.10
AN3-W	0.39	1.5	-0.66	0.42	3.84[de]	5.78	-1.54	0.26
AN3-G	1.05	3.25	0.35	1.34	4.75[fg]	7.10	-0.84	0.46
AN4-R	0.04	1.04	-1.17	0.16	6.04[ij]	9.06	-2.70	0.12
AN4-W	0.18	1.20	-1.06	0.21	3.13[cd]	4.79	-1.58	0.25
AN4-G	1.00	3.05	0.02	0.98	5.23[gh]	7.82	-1.04	0.39
AN5-R	0.03	1.03	-1.3	0.12	6.99[k]	10.56	-2.96	0.10
AN5-W	0.56	1.81	-0.79	0.34	3.82[de]	5.75	-1.30	0.31
AN5-G	1.15	3.69	0.06	1.02	5.29[ghi]	7.91	-0.82	0.47

Site (LSD)	0.43	0.68	0.63	0.59
Treatment (LSD)	0.25	NS	0.32	0.36
Site * treatment (LSD)	NS	NS	0.8	NS

Transformations of non-normal data for statistical analysis: [1] ((kgN_2O**-0.2)-1)/-0.2 [2] (((EF+0.044)**0.4)-1)/0.4 [3] ((yield t ha^{-1}**0.8)-1)/0.8 [4] ((yield-scaled emissions**-0.2)-1)/-0.2

865 **Table 5.** The impact of the nitrification inhibitor Dicyandiamide (DCD), site, fertiliser type and their interactions on annual cumulative N_2O emissions, EFs, grain yield, and
866 yield-scaled emissions: Transformed and back transformed values. When a significant effect is present, transformed values that do not share a letter are significantly different.
867 R = Rosemaund; W = Woburn; G = Gilchriston; AN = ammonium nitrate. Treatment rates are displayed in Table 2. Details of the transformations applied to normalise the
868 data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Site/treatment	Cumulative N_2O emissions (kg N_2O-N ha^{-1})		EF (%)		Grain yield (t ha^{-1})		Yield-scaled emissions (g N_2O-N kg^{-1} DM)	
	Transformed[1]	Back transformed	Transformed[2]	Back transformed	Transformed[3]	Back transformed	Transformed[4]	Back transformed
R	-0.07	0.93	-1.02	0.11	2.85	9.54	-1.67^{a}	0.10
W	0.10	1.10	-0.89	0.17	1.94	5.15	-1.23^{b}	0.22
G	0.76	1.98	-0.20	0.62	2.32	6.73	-1.02^{b}	0.30
AN	0.37	1.42	-0.71	0.26	2.42	7.20	-1.27	0.20
Urea	0.16	1.17	-0.70	0.27	2.31	6.68	-1.34	0.18
DCD	0.12^{a}	1.13	-0.90	0.16	2.35	6.86	-1.39^{a}	0.17
No DCD	0.41^{b}	1.47	-0.51	0.38	2.39	7.05	-1.23^{b}	0.22
R-AN	-0.09	0.91	-1.05	0.09	2.88^{d}	9.72	-1.69	0.09
R-Urea	-0.05	0.95	-1.00	0.11	2.82^{d}	9.36	-1.65	0.10
W-AN	0.13	1.14	-0.89	0.17	2.07^{b}	5.65	-1.27	0.20
W-Urea	0.07	1.07	-0.90	0.16	1.81^{a}	4.69	-1.19	0.23
G-AN	1.06	2.51	-0.20	0.62	2.33^{c}	6.77	-0.86	0.37
G-Urea	0.45	1.53	-0.24	0.59	2.30^{bc}	6.63	-1.19	0.23
R-DCD	-0.16	0.85	-1.12	0.07	2.91^{c}	9.91	-1.74	0.09
R-No DCD	0.02	1.02	-0.92	0.15	2.79^{c}	9.18	-1.61	0.11
W-DCD	-0.10	0.90	-1.14	0.06	1.89^{a}	4.97	-1.33	0.18
W-No DCD	0.30	1.33	-0.64	0.30	2.00^{a}	5.38	-1.14	0.25
G-DCD	0.37	1.42	-0.47	0.41	2.25^{b}	6.41	-1.21	0.22
G-No DCD	1.14	2.67	0.04	0.85	2.38^{b}	7.01	-0.84	0.38
AN-DCD	0.07	1.07	-1.13^{a}	0.06	2.41	7.15	-1.43	0.15
AN-No DCD	0.66	1.83	-0.29^{b}	0.55	2.44	7.29	-1.11	0.26
Urea-DCD	0.01	1.01	-0.67^{ab}	0.28	2.29	6.59	-1.41	0.16
Urea-No DCD	0.31	1.35	-0.72^{a}	0.25	2.34	6.82	-1.28	0.20
R-AN-DCD	-0.24	0.78	-1.21	0.03	2.98	10.36	-1.80	0.08

R-AN-No DCD	0.07	1.07	-0.88	0.17	2.77	9.06	-1.58	0.12
R-Urea-DCD	-0.07	0.93	-1.03	0.10	2.84	9.48	-1.67	0.10
R-Urea-No DCD	-0.02	0.98	-0.97	0.13	2.81	9.30	-1.63	0.11
W-AN-DCD	-0.18	0.83	-1.33	-0.01	2.06	5.61	-1.46	0.15
W-AN-No DCD	0.44	1.51	-0.46	0.42	2.09	5.73	-1.09	0.27
W-Urea-DCD	-0.01	0.99	-0.96	0.13	1.71	4.35	-1.20	0.23
W-Urea-No DCD	0.15	1.16	-0.83	0.20	1.91	5.04	-1.19	0.23
G-AN-DCD	0.70	1.89	-0.85	0.18	2.27	6.50	-1.03	0.29
G-AN-No DCD	1.42	3.26	0.46	1.35	2.40	7.10	-0.69	0.46
G-Urea-DCD	0.05	1.05	0.35	1.20	2.23	6.32	-1.39	0.17
G-Urea-No DCD	0.86	2.15	-0.38	0.48	2.37	6.96	-0.99	0.31
Site (LSD)	NS		NS		0.24		0.27	
Type (LSD)	NS		NS		0.08		NS	
DCD (LSD)	0.26		0.35		0.08		0.15	
Site*type (LSD)	NS		NS		0.23		NS	
Site*DCD (LSD)	NS		NS		0.23		NS	
Type*DCD (LSD)	NS		0.49		NS		NS	
Site*type*DCD (LSD)	NS		NS		NS		NS	

Transformations of non-normal data for statistical analysis [1] ((kgN_2O**0.3)-1)/0.3 [2] (((EF+0.19)**0.3)-1)/0.3 [3] ((yield t ha^{-1}**0.2)-1)/0.2 [4] ((yield scaled emissions**0.3)-1)/0.3

Table 6. The impact of additional splits of AN fertiliser application, site and their interaction on annual cumulative N_2O emissions, EFs, grain yield, and yield-scaled emissions: Transformed and back transformed values. When a significant effect is present, transformed values that do not share a letter are significantly different. R = Rosemaund; W = Woburn; G = Gilchriston; AN = ammonium nitrate. Treatment rates are displayed in Table 2. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Site/treatment	Cumulative N_2O emissions (kg N_2O-N ha^{-1})		EF (%)		Grain yield (t ha^{-1})		Yield-scaled emissions (g N_2O-N kg^{-1} DM)	
	Transformed[1]	Back transformed	Transformed[2]	Back transformed	Transformed[3]	Back transformed	Transformed[4]	Back transformed
R	-0.03[a]	0.97	-1.77[a]	0.11	7.25[a]	9.42	-1.64[a]	0.10
W	0.32[a]	1.38	-0.93[a]	0.36	4.25[b]	5.75	-1.14[b]	0.25
G	1.06[b]	3.07	0.16[b]	1.17	5.23[c]	6.93	-0.72[c]	0.44
AN	0.52[a]	1.71	-0.72[a]	0.46	5.54	7.30	-1.12	0.26
AN split	0.38[b]	1.47	-0.98[b]	0.34	5.61	7.39	-1.21	0.22
AN-R	0.05	1.05	-1.63	0.14	6.97	9.07	-1.58	0.12
AN split-R	-0.10	0.91	-1.92	0.09	7.53	9.77	-1.70	0.09
AN-W	0.40	1.50	-0.80	0.42	4.29	5.79	-1.09	0.27
AN split-W	0.25	1.29	-1.07	0.30	4.21	5.70	-1.19	0.23
AN-G	1.12	3.28	0.28	1.31	5.37	7.10	-0.69	0.46
AN split-G	1.00	2.87	0.05	1.05	5.09	6.76	-0.75	0.43
Site (LSD)	0.46		0.89		0.93		0.23	
Treatment (LSD)	0.11		0.18		NS		NS	
Site * treatment (LSD)	NS		NS		NS		NS	

Transformations of non-normal data for statistical analysis: [1] ((gN_2O/1000)**-0.1)-1)/-0.1 [2]((EF**0.2)-1)/0.2 [3] ((yield t ha^{-1}**0.9)-1)/0.9 [4] ((yield scaled emissions**0.3)-1)/0.3

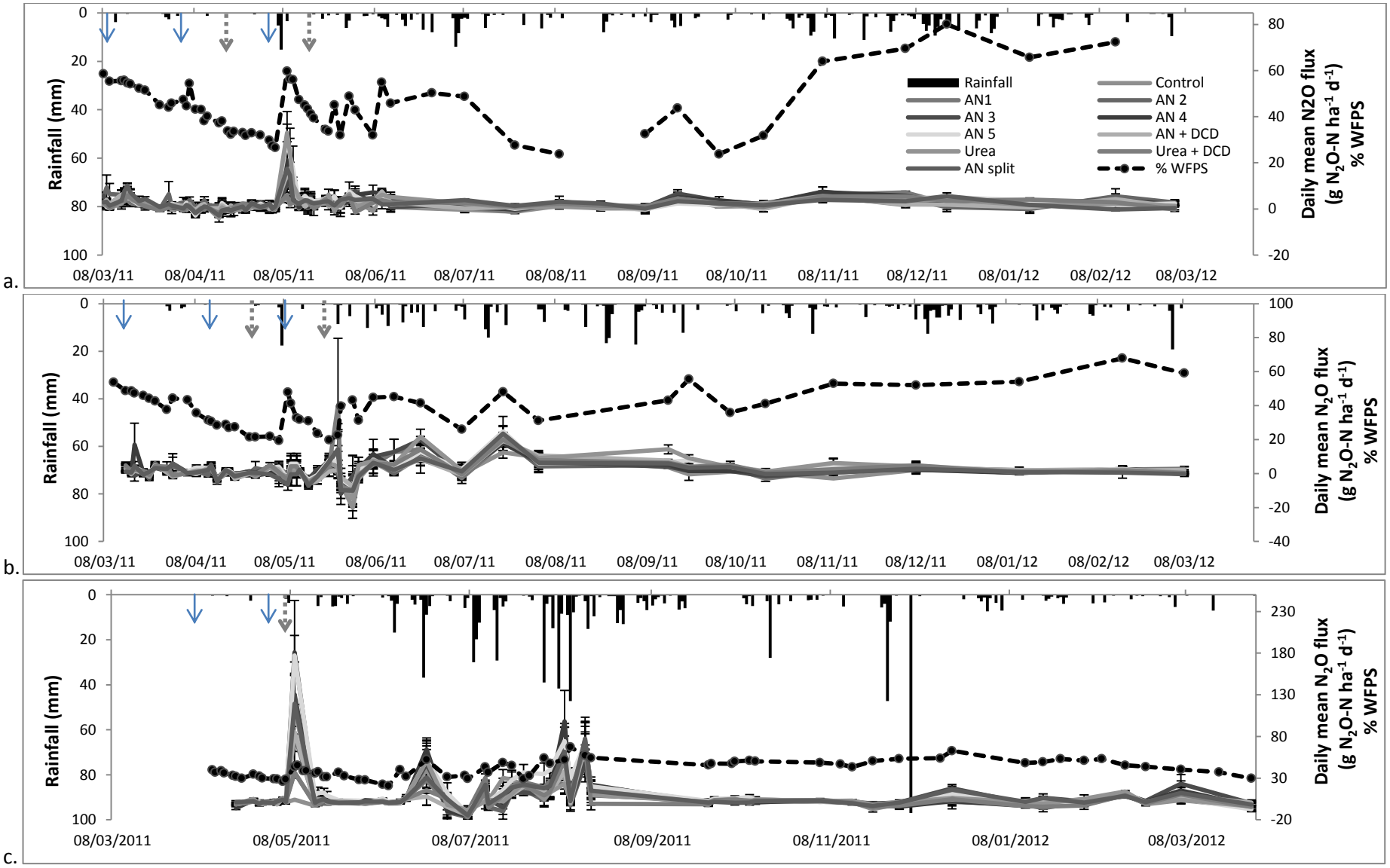
Figure Captions

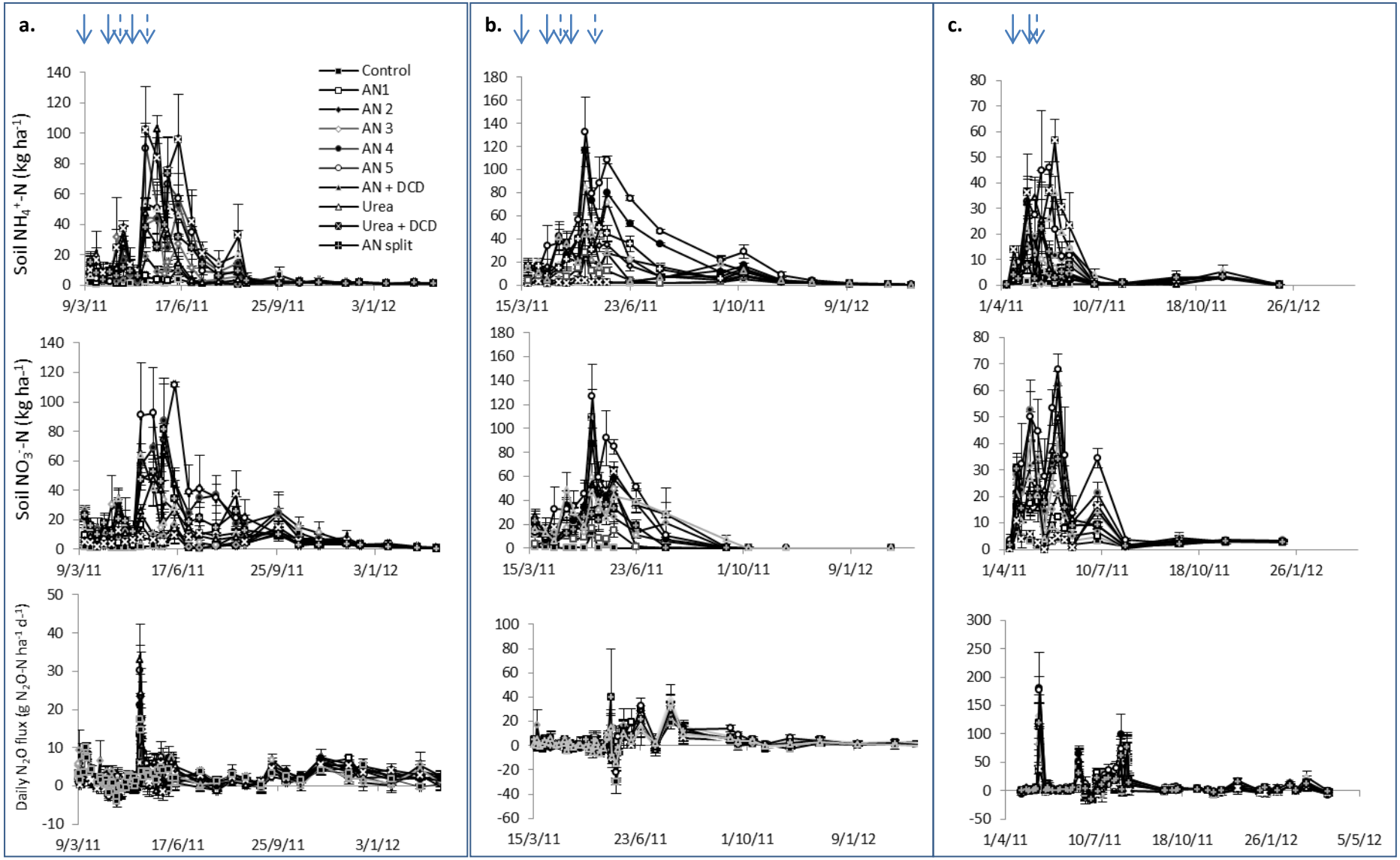
Fig. 1. Daily variation in N_2O emissions, rainfall and %WFPS at **a.** Rosemaund; **b.** Woburn; **c.** Gilchriston. Solid arrows represent times of fertiliser application; dashed arrows indicate the timing of additional doses applied in AN split treatments. (Note different Y axes for Daily Mean N_2O flux and %WFPS between a, b and c). Error bars represent the SE of the mean.

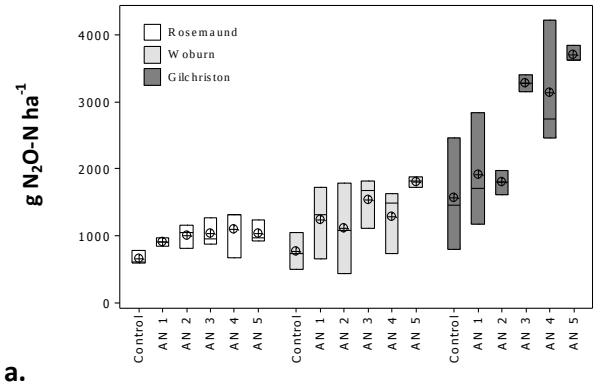
Fig. 2. Annual variation in soil NH_4^+-N, soil NO_3^--N contents and N_2O emissions at: **a.** Rosemaund; **b.** Woburn; **c.** Gilchriston. Solid arrows represent times of fertiliser application; dashed arrows indicate the timing of additional doses applied in AN split treatments. (Note different Y axes between a, b and c).

Fig. 3a. Variation in measured annual cumulative N_2O emissions for all rates of AN fertiliser at each of the three arable sites (n = 3); **b.** Variation in measured EFs for all rates of AN fertiliser at each of the three arable sites (n = 3. Two outliers removed from analysis from Gilchriston AN1, one outlier removed from Gilchriston AN2); **c.** Variation in measured yield-scaled emissions for all rates of AN fertiliser at each of the three arable sites (n = 3). Fertiliser descriptions are contained in Table 2. Crossed circles represent the mean, horizontal lines represent the median, vertical boxes represent the interquartile range.

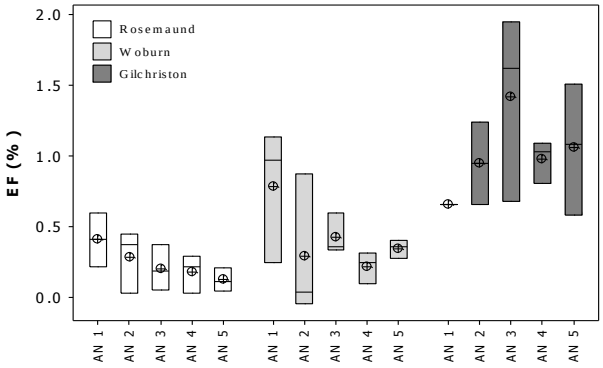
Fig. 4a. Variation in measured annual cumulative N_2O emissions for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3); **b.** Variation in measured EFs for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3. Two outliers removed from analysis from Gilchriston Urea + DCD); **c.** Variation in measured grain yield for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3); **d.** Variation in measured yield-scaled emissions for AN and urea fertiliser with/without DCD and AN split applications at the three arable sites (n = 3). Fertiliser descriptions are contained in Table 2. Crossed circles represent the mean, horizontal lines represent the median, vertical boxes represent the interquartile range


a.
Rainfall (mm)
Daily mean N2O flux (g N2O-N ha-1 d-1)
% WFPS
Rainfall
AN1
AN 3
AN 5
Urea
AN split
Control
AN 2
AN 4
AN + DCD
Urea + DCD
% WFPS
08/03/11
08/04/11
08/05/11
08/06/11
08/07/11
08/08/11
08/09/11
08/10/11
08/11/11
08/12/11
08/01/12
08/02/12
08/03/12
b.
Rainfall (mm)
Daily mean N2O flux (g N2O-N ha-1 d-1)
% WFPS
08/03/11
08/04/11
08/05/11
08/06/11
08/07/11
08/08/11
08/09/11
08/10/11
08/11/11
08/12/11
08/01/12
08/02/12
08/03/12
c.
Rainfall (mm)
Daily mean N2O flux (g N2O-N ha-1 d-1)
% WFPS
08/03/2011
08/05/2011
08/07/2011
08/09/2011
08/11/2011
08/01/2012
08/03/2012

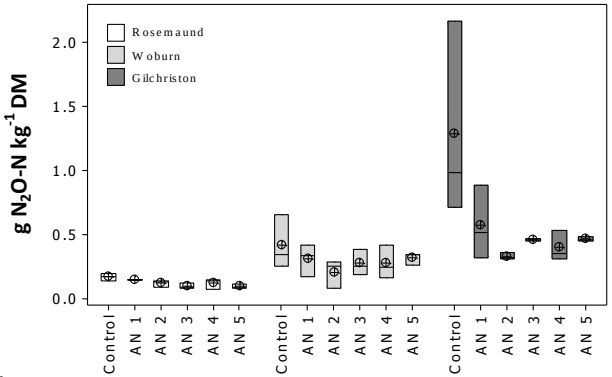

a.
b.
c.
Control
AN1
AN 2
AN 3
AN 4
AN 5
AN + DCD
Urea
Urea + DCD
AN split
Soil NH4+-N (kg ha-1)
Soil NO3--N (kg ha-1)
Daily N2O flux (g N2O-N ha-1 d-1)
9/3/11
17/6/11
25/9/11
3/1/12
15/3/11
23/6/11
1/10/11
9/1/12
1/4/11
10/7/11
18/10/11
26/1/12
5/5/12


Rosemaund
Woburn
Gilchriston
g N2O-N ha-1
0
1000
2000
3000
4000
Control
AN 1
AN 2
AN 3
AN 4
AN 5

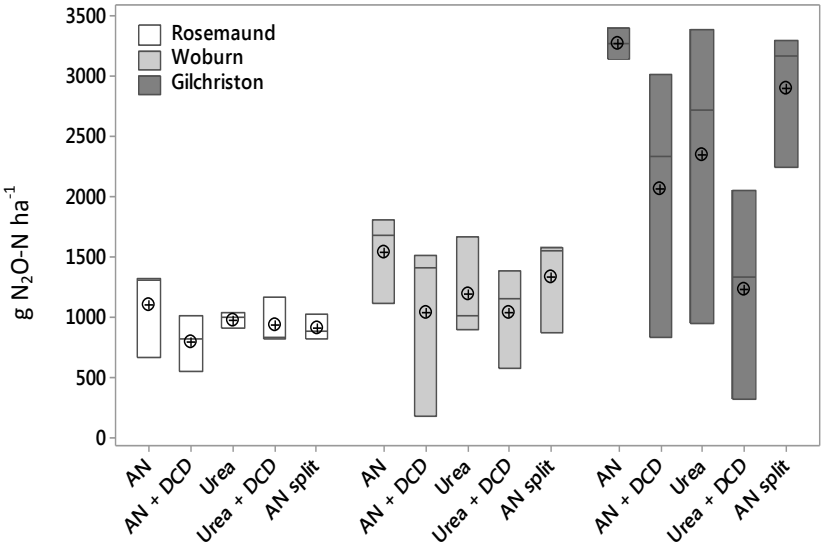
a.


Rosemaund
Woburn
Gilchriston
EF (%)
0.0
0.5
1.0
1.5
2.0
AN 1
AN 2
AN 3
AN 4
AN 5

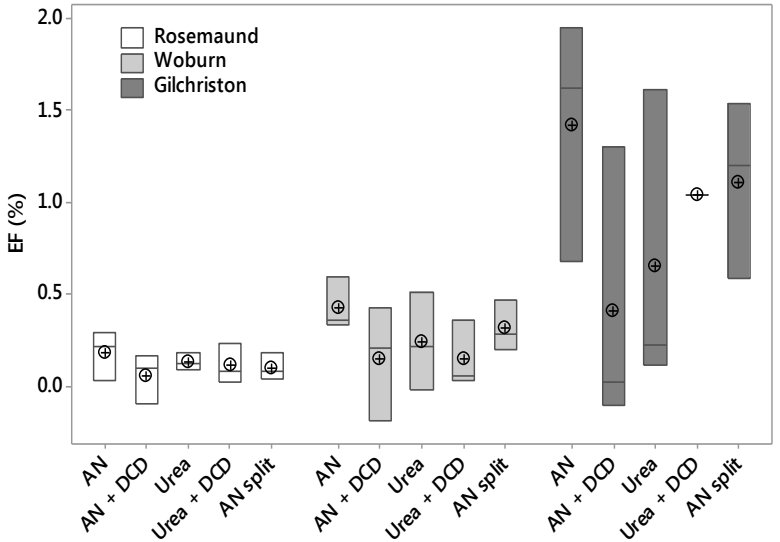
b.


Rosemaund
Woburn
Gilchriston
g N2O-N kg-1 DM
0.0
0.5
1.0
1.5
2.0
Control
AN 1
AN 2
AN 3
AN 4
AN 5

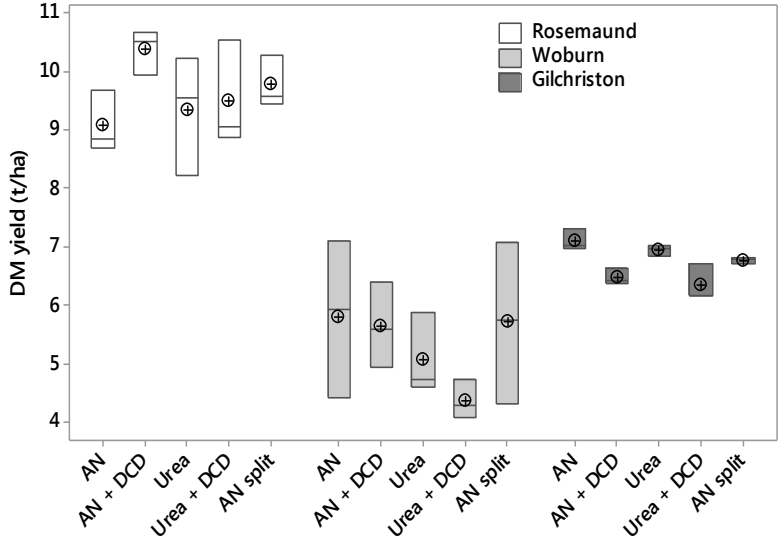
c.


Rosemaund
Woburn
Gilchriston
g N_2O-N ha^{-1}
3500
3000
2500
2000
1500
1000
500
0
AN
AN + DCD
Urea
Urea + DCD
AN split

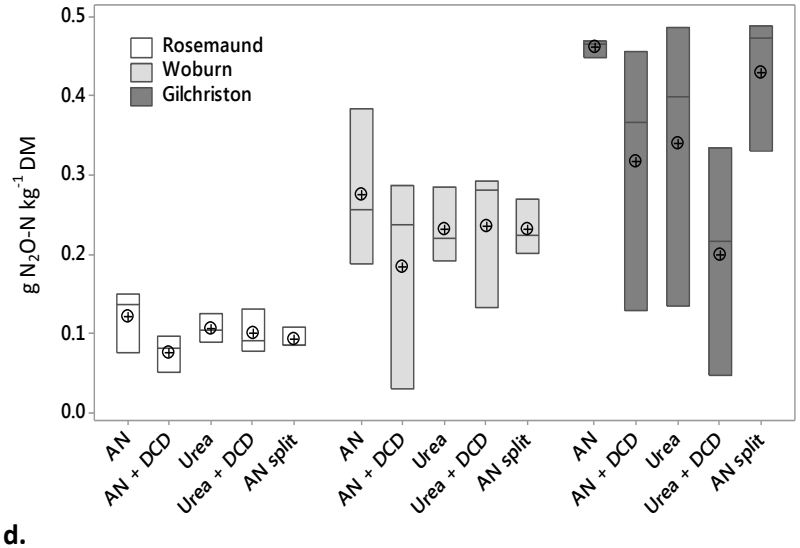
a.


Rosemaund
Woburn
Gilchriston
EF (%)
2.0
1.5
1.0
0.5
0.0
AN
AN + DCD
Urea
Urea + DCD
AN split

b.


Rosemaund
Woburn
Gilchriston
DM yield (t/ha)
11
10
9
8
7
6
5
4
AN
AN + DCD
Urea
Urea + DCD
AN split

c.


Rosemaund
Woburn
Gilchriston
g N_2O-N kg^{-1} DM
0.5
0.4
0.3
0.2
0.1
0.0
AN
AN + DCD
Urea
Urea + DCD
AN split

d.

Supplementary Table 1. Annual cumulative N_2O emissions: The mean and standard error (SE) for all fertiliser treatments at each of the arable sites (before removal of outliers and data transformation for statistical analysis). Treatment rates are displayed in Table 2.

	Rosemaund mean (g N_2O-N ha^{-1})	Rosemaund SE (g N_2O-N ha^{-1})	Woburn mean (g N_2O-N ha^{-1})	Woburn SE (g N_2O-N ha^{-1})	Gilchriston mean (g N_2O-N ha^{-1})	Gilchriston SE (g N_2O-N ha^{-1})
Control	666	59	766	154	1572	480
AN1	912	39	1236	311	1908	490
AN2	1008	100	1109	387	1796	105
AN3	1033	120	1539	214	3271	74
AN4	1102	215	1289	277	3137	540
AN5	1041	98	1807	43	3691	70
An split	910	59	1334	232	2904	330
Urea	981	38	1194	239	2351	730
AN + DCD	796	134	1036	432	2061	643
Urea+DCD	937	112	1036	242	1237	502

Supplementary Table 2. Annual emission factors (EFs): The mean and standard error (SE) for all fertiliser treatments at each of the arable sites (before removal of outliers and data transformation for statistical analysis). Treatment rates are displayed in Table 2.

	Rosemaund mean (%)	Rosemaund SE (%)	Woburn mean (%)	Woburn SE (%)	Gilchriston mean (%)	Gilchriston SE (%)
AN1	0.41	0.11	0.78	0.27	0.84	2.39
AN2	0.29	0.13	0.29	0.29	0.28	0.69
AN3	0.2	0.09	0.43	0.08	1.42	0.38
AN4	0.18	0.08	0.22	0.06	0.98	0.09
AN5	0.13	0.05	0.35	0.03	1.06	0.27
An split	0.10	0.04	0.32	0.08	1.11	0.28
Urea	0.13	0.03	0.24	0.16	0.65	0.48
AN + DCD	0.05	0.08	0.15	0.18	0.41	0.45
Urea+DCD	0.11	0.06	0.15	0.10	-0.28	0.66

Supplementary Table 3. Annual grain yield: The mean and standard error (SE) for all fertiliser treatments at each of the arable sites (before removal of outliers and data transformation for statistical analysis). Treatment rates are displayed in Table 2.

	Rosemaund mean (t ha^{-1})	Rosemaund SE (t ha^{-1})	Woburn mean (t ha^{-1})	Woburn SE (t ha^{-1})	Gilchriston mean (t ha^{-1})	Gilchriston SE (t ha^{-1})
Control	3.95	0.29	1.92	0.17	1.24	0.11
AN1	6.23	0.31	3.94	0.10	3.39	0.14
AN2	8.49	0.51	5.23	0.53	5.42	0.15
AN3	10.28	0.05	5.81	0.78	7.10	0.10
AN4	9.06	0.31	4.80	0.62	7.82	0.05
AN5	10.56	0.37	5.76	0.55	7.91	0.05
An split	9.77	0.26	5.71	0.80	6.76	0.03
Urea	9.33	0.58	5.06	0.58	6.94	0.06
AN + DCD	10.37	0.22	5.65	0.42	6.48	0.08
Urea+DCD	9.49	0.53	4.37	0.19	6.34	0.18

Supplementary Table 4. Yield-scaled emissions: The mean and standard error (SE) for all fertiliser treatments at each of the arable sites (before removal of outliers and data transformation for statistical analysis). Treatment rates are displayed in Table 2.

	Rosemaund mean ($g\ N_2O\text{-}N\ kg^{-1}$ DM)	Rosemaund SE ($g\ N_2O\text{-}N\ kg^{-1}$ DM)	Woburn mean ($g\ N_2O\text{-}N\ kg^{-1}$ DM)	Woburn SE ($g\ N_2O\text{-}N\ kg^{-1}$ DM)	Gilchriston mean ($g\ N_2O\text{-}N\ kg^{-1}$ DM)	Gilchriston SE ($g\ N_2O\text{-}N\ kg^{-1}$ DM)
Control	0.17	0.02	0.42	0.12	1.29	0.44
AN1	0.15	0.00	0.31	0.07	0.58	0.17
AN2	0.12	0.02	0.21	0.06	0.33	0.02
AN3	0.10	0.01	0.28	0.06	0.46	0.01
AN4	0.12	0.02	0.28	0.08	0.40	0.07
AN5	0.10	0.01	0.32	0.03	0.47	0.01
An split	0.09	0.01	0.23	0.02	0.43	0.05
Urea	0.11	0.01	0.23	0.03	0.34	0.10
AN + DCD	0.08	0.01	0.19	0.08	0.32	0.10
Urea+DCD	0.10	0.02	0.24	0.05	0.20	0.08